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(72) Proprietor: MOBIL OIL CORPORATION
150 East 42nd Street
New York New York 10017 (US)

(72) Inventor: Rudnick, Leslie Robert
5 Winthrop Road
Lawrenceville New Jersey 08648 (US)

(74) Representative: Cooper, John Anthony et al
Mobil Court 3 Clements Inn
London WC2A 2EB (GB)

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Description

This invention relates to the processing of residual petroleum charge stocks by visbreaking in the presence of certain highly aromatic hydrogen-donor materials.

Visbreaking, or viscosity breaking, is a well-known petroleum refining process in which reduced crudes are pyrolyzed, or cracked, under comparatively mild conditions to provide products having lower viscosities and pour points, thus reducing the amounts of less-viscous and more valuable blending oils required to make the residual stocks useful as fuel oils. The visbreaker feedstock usually consists of a mixture of two or more refinery streams derived from sources such as atmospheric residuum, vacuum residuum, furfural-extract, propane-deasphalted tar and catalytic cracker bottoms. Most of these feedstock components, except the heavy aromatic oils, behave independently in the visbreaking operation. Consequently, the severity of operation for a mixed feed is limited greatly by the least desirable (highest coke forming) components. In a typical visbreaking process, the crude or resid feed is passed through a heater and heated to about 425 to about 525°C and at about 450 to about 7000 kPa. Light gas-oil may be recycled to lower the temperature of the effluent to about 260 to about 370°C. Cracked products from the reaction are flash distilled with the vapor overhead being fractionated into a light distillate overhead product, for example gasoline and light gas-oil bottoms, and the liquid bottoms being vacuum fractionated into heavy gas-oil distillate and residual tar. Examples of such visbreaking methods are described in Beuther et al, "Thermal Visbreaking of Heavy Residues," *The Oil and Gas Journal*, 57:46, November 9, 1959, pp. 151—157; Rhoe et al, "Visbreaking: A Flexible Process," *Hydrocarbon Processing*, January 1979, pp. 131—136; and United States Patent 4,233,138.

Various visbreaking processes have been proposed in which residual oils are added to the visbreaking stage with or without added hydrogen or hydrogen-donors. For example, U.S. Patent 3,691,058 describes the production of single ring aromatic hydrocarbons (70—220°C) by hydrocracking a heavy hydrocarbon feed (565°C—) and recycling 32—70°C and 220°C+ product fractions to extinction. This is integrated with visbreaking of residua in the presence of 1—28 weight % free radical acceptor at 370 to 480°C in the presence or absence of hydrogen (to enhance residua depolymerization). U.S. Patent 4,067,757 describes a process comprising passing a resid up through a bed of inertia solids (packed bed reactor) in the presence or absence of 9—1800 Nm³ hydrogen per m³ resid at 400 to 540°C to enhance the production of middle distillate (175—345°C).

U.S. Patent 2,953,513 proposes the production of hydrogen-donors by partial hydrogenation of certain distillate thermal and catalytic tars, boiling above 370°C, containing a minimum of 40 weight % aromatics, to contain H/C ratios of 0.7—1.6. The resid feed is then mixed with 9—83 volume % of hydrogen-donor and thermally cracked at 427—482°C to produce low boiling products. U.S. Patent 4,090,947 describes a thermal cracking process (425—540°C) for converting resids into lighter products in the presence of 10—500 volume % hydrogen-donor. The hydrogen-donor is produced by hydrotreating premium coker gas oil (345—480°C) alone or blended with gas oil produced in the thermal cracker. U.S. Patent 4,292,168 proposes upgrading heavy hydrocarbon oils without substantial formation of chat by heating the oil with hydrogen and a hydrogen transfer solvent without a catalyst at temperatures of about 320—500°C and a pressure of 2200—18000 kPa for a time of about 3—30 minutes. Examples of hydrogen-donor transfer solvents include pyrene, fluoranthene, anthracene and benzanthracene. U.S. Patent 4,292,686 describes a process for contacting a resid with a hydrogen-donor at 350—500°C and a pressure of 2—7 MPa with liquid hourly space velocities ranging from 0.5—10.

European Patent Application 133,774 describes a process for the production of fuel oil products in which the formation of coke or filtration sediment is suppressed by visbreaking heavy petroleum residua under liquid phase, non-catalytic conditions in the presence of certain hydrogen-donor materials and in the absence of added free hydrogen. By means of the invention described in that application, heavy petroleum oil feed stocks containing deleterious contaminants such as sulfur and nitrogen compounds, asphaltenes and metals, can be visbroken at high severities to provide lower molecular weight fuel oil products of improved viscosity and pour point characteristics. The process of that invention offers the potential of substantially eliminating and/or reducing the need for cutter stock to meet fuel oil product viscosity specifications.

The present invention represents an improvement in the visbreaking process described in that application and involves introducing an organic sulfur compound into the heavy petroleum residual oil before it is subjected to visbreaking in the presence of a hydrogen donor material.

According to the invention, therefore, there is provided a process for visbreaking a heavy petroleum residual oil comprising:

- (a) add to the residual oil an organic sulfur compound having an active thiol component; and
- (b) visbreaking the residual oil in the presence of a highly aromatic hydrogen donor material having a content of H_A, and H_{alpha} hydrogen each of at least 20 percent of the total hydrogen-donor hydrogen content, and recovering a fuel oil product having a viscosity lower than that of the starting residual oil.

The hydrogen-donor material used in the process of the invention is a thermally stable, polycyclic aromatic of hydroaromatic distillate mixture which results from one or more petroleum refining operations. The hydrogen-donor preferably has an average boiling point in the range of 230 to 510°C and an A.P.I. gravity below 20°C.

Examples of suitable hydrogen-donors are highly aromatic petroleum refinery streams, such as fluidized catalytic cracker (FCC) "main column" bottoms, FCC "light cycle oil," and thermofor catalytic cracker (TCC) "syntower" bottoms, all of which contain a substantial proportion of polycyclic aromatic hydrocarbon constituents such as naphthalene, dimethylnaphthalene, anthracene, phenanthrene, fluorene, chrysene, pyrene, perylene, diphenyl, benzothiophene, tetralin and dihydronaphthalene, for example. Such refractory petroleum materials are resistant to conversion into higher (lower molecular weight) products by conventional non-hydrogenative procedures. Typically, these petroleum refinery residual and recycle fractions are hydrocarbonaceous mixtures having an average carbon to hydrogen ratio above about 1:1, and an average boiling point above 230°C.

An FCC main column bottoms refinery fraction is a highly preferred donor for use in the process of the invention. A typical FCC main column bottoms (or FCC clarified slurry oil (CSO)) contains a mixture of constituents as represented in the following mass spectrometric analysis:

Compounds	Aromatics	Naphthenic/ Aromatics	Labile H ₂ %
Alkyl-Benzene	0.4	—	0.00
Naphthene-Benzenes	—	1.0	0.03
Dinaphthene-Benzenes	—	3.7	0.16
Naphthalenes	0.1	—	0.00
Acenaphthenes (biphenyls)	—	7.4	0.08
Fluorenes	—	10.1	0.11
Phenanthrenes	13.1	—	—
Naphthene-phenanthrenes	—	11.0	0.18
Pyrenes, fluoroanthenes	20.5	—	0
Chrysenes	10.4	—	0
Benzofluoranthenes	6.9	—	0
Perylenes	5.2	—	0
Benzothiophenes	2.4	—	—
Dibenzothiophenes	2.4	—	—
Naphthobenzothiophenes	—	2.4	—
TOTAL	64.4	35.6	0.60

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A typical FCC main column bottoms or clarified slurry oil has the following analysis and properties:

	Elemental Analysis, wt. %	
5	C	89.93
	H	7.35
	O	0.99
10	N	0.44
	S	1.09
15	TOTAL	99.80
	Pour Point, °C: 10	
20	COR, % : 9.96	
	Distillation	
	IBP, °C : 254	
25	5%, °C : 338	
	95%, °C : 485	

30 Another preferred hydrogen-donor material is a light cycle oil (LCO) taken from the main tower fractionator in a FCC operation of the riser type in which the LCO results from a distillation cut point not substantially above about 370°C.

A typical FCC light cycle oil (LCO) has the following analysis and properties:

35	FCC LCO	
	Boiling Point Distribution, wt. %	
	215°C	4.8
40	215—343°C	87.9
	343—427°C	7.3
	427—538°C	—
	538°C+	—
45	H, wt. %	10.64
	S, wt. %	1.01
	N, wt. %	0.24
	Ni + V, PRM	—
50	COR, wt. %	—
	Paraffins, wt. %	12.7
	Mononaphthenes	11.7
55	Polynaphthenes	12.8
	Monoaromatics	24.7
	Diaromatics	21.7
	Polyaromatics	14.3
60	Aromatic sulfur type	2.1
	Total hydrogen, wt. %	9.0—9.5

65 FCC main tower bottoms and light cycle oils are obtained by the catalytic cracking of gas oil in the

presence of a solid porous catalyst. More complete descriptions of the production of these petroleum fractions can be found in U.S. Patents 3,725,240 and 4,302,323, for example.

Catalytically cracked stocks such as clarified slurry oils and light cycle oils are preferred hydrogen-donor materials because of their unique physical properties and chemical constituents. A critical aspect of the hydrogen-donor material is the particular proportions of aromatic naphthenic and paraffinic moieties and the type and content of aromatic and naphthenic structures together with a high content of alpha hydrogen provides a superior hydrogen-donor material.

The hydrogen transfer ability of a donor material can be expressed in terms of specific types of hydrogen content as determined by proton nuclear magnetic resonance spectral analysis. Nuclear magnetic resonance characterization of heavy hydrocarbon oils is well developed. The spectra 60 (c/sec) are divided into four bands (H_{α} , H_{β} , H_{γ} and H_{Ar}) according to the following frequencies in Hertz (Hz) and chemical shift (delta):

	H_{α}	H_{β}	H_{γ}	H_{Ar}
Hz	0—60	60—100	120—200	360—560
delta	0—1.0	1.0—1.8	2.0—3.3	6.0—9.2

The H_{Ar} protons are attached to aromatic rings and are a measure of aromaticity of a material. H_{α} protons are attached to non-aromatic carbon atoms themselves attached directly to an aromatic ring structure, e.g., alkyl groups and naphthenic ring structures. H_{β} protons are attached to carbon atoms which are in a second position away from an aromatic ring, and H_{γ} protons are attached to carbon atoms which are in a third position or more away from an aromatic ring structure. This can be illustrated by the compounds shown in the accompanying drawing (Fig. 1).

The H_{Ar} protons are important because of their strong solvency power. A high content of H_{α} protons is particularly significant because H_{α} protons are labile and are potential hydrogen-donors.

It is particularly preferred that the hydrogen-donor material used in the process of the invention has a hydrogen content distribution in which the H_{Ar} proton content is from 20 to 50 percent and the H_{α} proton content is at least 20 percent, preferably from 20 to 50 percent. For example, in H-donor streams containing 9.5 weight % total hydrogen, the alpha-hydrogen content should be at least 1.9 wt. % (20% of total hydrogen content). The balance of the hydrogen is non-alpha hydrogen.

Hydrogen-donors possessing the desired hydrogen content distribution can be obtained as a bottoms fraction from the catalytic or hydrocracking of gas oil stocks in the moving bed or fluidized bed reactor processes. In general, depending upon such conditions as temperature, pressure, catalyst-to-oil ratio, space velocity and catalyst nature, a high severity cracking process results in a petroleum residuum solvent having an increased content of H_{Ar} and H_{α} protons and a decreased content of the less desirable non-alpha hydrogen.

The proton distribution in examples of various highly aromatic hydrocarbon by-product streams is shown below.

Example	H_{α} (weight %)	Non-alpha Hydrogen (weight %)	H_{Ar} (weight %)	H Total (weight %)
<u>FCC/LCO</u>				
#1	22.2 (2.07)	57.8	20.0	9.34
#2	34.1 (3.18)	36.8	29.1	9.32
#3	34.3 (3.19)	35.5	30.2	9.30
(Note the values in () are absolute percentage amounts and all three LCO streams are effective H-donors.)				
<u>FCC/Clarified Slurry Oil</u>				
#1	34.0 (2.43)	33.0	33.0	7.15
#2	30.0 (2.15)	35.0	35.0	7.17
#3	19.4 (2.15)	65.0	5.0	7.16

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	Example	H _{alpha} (weight %)	Non-alpha Hydrogen (weight %)	H _{Ar} (weight %)	H Total (weight %)
5	<u>FCC/Main Column Bottoms</u>				
	#1	36.0 (2.65)	32.0	32.0	
10	#2	36.4 (2.68)	18.8	44.8	
	#3	18.5 (1.36)	64.3	17.2	
	#4	18.1 (1.33)	67.7	14.2	
15	<u>TCC/Syntower Bottoms</u>				
	#1	29.8 (2.78)	28.8	41.4	
20	#2	18.2 (1.70)	58.8	23.0	
	#3	16.3 (1.52)	68.1	15.6	
	<u>SRC Recycle</u>				
25	Oil	27.1	21.6	46.3	
	<u>TCC Distillate</u>				
30	#1	21.5 (2.39)	58.4	20.1	
	#2	20 (2.07)	58	22	
	#3	6.9 (0.89)	85.1	8	
35					

All of the values reported above are for non-hydrotreated materials.

From the data given above, it will be seen that hydrocarbons having the same general process deviation may or may not have the desired proton distribution. For example, FCC/MCB #1 and #2 and FCC/CSO #1 and #2 have the desired proton distribution while FCC/MCB #3 and #4 and FCC/CSO #3 do not. Furthermore, although it is preferred that the highly aromatic hydrogen donor component is derived from petroleum, it will be noted that the SRC recycle solvent closely resembles FCC/MCB #1 and #2.

The organic sulfur compound which is introduced into the residuum to be subjected to visbreaking is preferably one in which there is present an active thiol (—SH) group. Suitable compounds in this respect include thiophenol, dodecanethiol and benzothiophene. Dibenzothiophene, on the basis of present knowledge, is not a suitable sulfur compound.

In addition, refinery streams obtained from the extraction of paraffinic oils to remove aromatics, for example with furfural, and other refinery streams can contain sufficient sulfur compounds having sufficient thiol functionality and can be added to the residuum, directly or indirectly.

Another method of introducing the organic sulfur compound into the heavy residuum is to sulfonate the aromatic extract derived from extracting a paraffinic oil with phenol or furfural, for example to remove aromatic compounds; the sulfonated aromatics are then mildly hydrogenated to form the organic sulfur compound suitable for addition to heavy residua for visbreaking. Techniques for aromatic extraction, sulfonation, and hydrogenation are well known in the art.

Still another source of thiol compounds is the extract obtained by contacting a hydrocarbon stream containing thiophenols with an alkaline solution, such as sodium hydroxide in water or alcohol, decanting the alkaline phase, and then acidifying the solution to release the thiol compounds. The thiol compounds can be separated and mixed with the heavy residua. This technique provides a means for removing sulfur from one portion of a refinery stream and utilizing the sulfur in another part of the refinery process. Hydrocarbon streams that can be used in the manner include aromatic (furfural) extracts from lube oil stock and cycle oil stock.

The process of the invention is advantageously carried out in refinery facilities of the type shown diagrammatically in the accompanying drawing. Referring to the drawing (Fig. 2), a viscous hydrocarbon oil feed, typified by a 496°C+ Arab Heavy resid, is supplied by line 4 to visbreaking heater 8. The feed is blended with hydrogen donor materials supplied through line 6 in an amount from 0.1 to 50 weight

percent, preferably from 0.1 to 20 weight percent based on the resid charge (a weight ratio of hydrogen-donor to resid of 0.001 to 0.5, preferably 0.001 to 0.2). Organic sulfur compounds are added through line 2 to provide an amount equivalent to 0.05 to 10 percent by weight of sulfur in the stream flowing to line 2. Preferably the amount added is equivalent to from 0.5 to 5 percent sulfur. Mild thermal cracking of the resid under visbreaking conditions occurs in visbreaker 8 and produces a visbreaker effluent stream carried by line 10. This stream is cooled by admixture with a quench stream from line 14, and the visbreaker effluent continues through line 12 to distillation column 22 where it is fractionated to obtain C_2 -gases (C_2 , C_3 and lower) and a C_6 -135°C naphtha fraction from the top through line 24. A 220°C+ fraction is taken off as a bottoms stream through line 16 where portions may be recycled as a quench stream through line 14, recovered as heavy fuel oil through line 18 or, via line 20, blended with cutter stock to meet fuel oil product specifications.

The overhead fraction removed from the distillation column in line 24 is passed through a cooler separator 26 which is operated under conditions effective to separate the incoming liquid into a C_6 -off-gas stream 28, mainly C_2 or C_3 and lower, and a C_6 -135°C naphtha fraction which is taken off via line 30. Because of the quality of the hydrogen-donor, it can be removed in admixture with the heavy oil fraction and used directly as heavy fuel oil, thus avoiding the need for separation.

The process of the invention is suitable for upgrading a wide variety of heavy liquid hydrocarbon oils in which mixtures of at least 75 weight percent of the components boil over 370°C. Included in this class of materials are residual fractions obtained by catalytic cracking of gas oils, solvent extracts obtained during the processing of lube oil stocks, asphalt precipitates obtained from deasphalting operations, high boiling bottoms or resids obtained during vacuum distillation of petroleum oils and tar sand bitumen feedstocks.

Visbreaking process conditions can vary widely based on the nature of the heavy oil material, the hydrogen-donor material and other factors. In general, the process is carried out at temperatures ranging from 350 to 485°C, preferably 425 to 455°C, at residence times ranging from 1 to 60 minutes, preferably 7 to 20 minutes. The pressures employed will be sufficient to maintain liquid phase conditions usually 1480 to 7000 kPa.

An important aspect of the invention is the improvement of visbreaker performance by optimizing operation severity for heavy oil feedstocks. In general, as severity increased, increased yields of distillate and gaseous hydrocarbons are obtained with a reduction in the amount of cutter oil required for blending to obtain specification-viscosity residual fuel oil. At high severities, however, there is an increased tendency to form coke deposits which result in plugged heater tubes and/or the production of unstable fuel oils as measured by sediment formation. By means of the process of the invention, the use of certain hydrogen-donors in combination with certain organic sulfur compounds has been found to suppress the formation of sedimentation species and thus permit visbreaking at a higher severity consistent with the production of stable fuel oil. As an example, the visbreaking of a heavy petroleum feed stock conventionally carried out at, say, 427°C with a residence time of 500 seconds may be carried out at 427°C with a residence time of 800 seconds under the conditions of the invention to obtain a fuel oil product free of sedimenting species. At such higher severities, the current stock requirement is substantially reduced and this represents a considerable financial savings.

Example

The effectiveness of thiophenolic compounds in increasing the hydrogen donor capacity of a hydrogen donor solvent was demonstrated by the following tests.

Four tests were made utilizing heavy-wall glass tubes into which the materials shown in Column 2 of the following Table were added in the amounts shown in Column 3. The tubes were blanketed in nitrogen, sealed and heated at 440°C for 1 hour. The mixtures were then analyzed using vapor pressure chromatography and the hydrogen-donor capacity of each mixture was calculated.

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TABLE

	1	2	3	4	5
	Run No.	Compounds	Weight, gms	Weight % Sulfur	H-donorCapacity
6	1	Durban Clarified			
		Slurry Oil	0.2311	4.83	0.893
10		benzophenone	0.2007		
	2	Clarified			
15		Slurry oil	0.2093	0.95	1.16
		benzophenone	0.2026		
20	3	Clarified			
		Slurry oil	0.2110	0.95	4.81
		thiophenol	0.4311	3.88	
25		benzophenone	0.2011	—	
	4	Clarified			
30		Slurry oil	0.2069	0.95	0.876
		dibenzothiophene	0.0770	3.88	
35		benzophenone	0.2019	—	

Claims

1. A process for visbreaking a heavy petroleum residual oil comprising:
 - (a) adding to the residual oil an organic sulfur compound having an active thiol component before
 - (b) visbreaking the residual oil in the presence of a highly aromatic hydrogen donor material having a content of H_{Ar} and H_{Alpha} hydrogen of at least 20 percent of the total hydrogen-donor hydrogen content, and recovering a fuel oil product having a viscosity lower than that of the starting residual oil.
2. A process according to Claim 1, wherein the H_{Ar} hydrogen content is from 20 to 50 percent and the H_{Alpha} hydrogen content is from 20 to 50 percent, based on total hydrogen content.
3. A process according to Claim 2, wherein the hydrogen donor solvent has a H_{Alpha} content of at least 1.9 weight % and H_{Ar} content of at least 2.0 weight %.
4. A process according to any one of Claims 1 to 3, wherein the hydrogen-donor material is an FCC main column bottoms, a clarified slurry oil, a TCC syntower bottoms, an SRC recycle oil or a light cycle oil.
5. A process according to any one of Claims 1 to 4, wherein visbreaking is carried out at a temperature from 350 to 485°C and for a residence time from 1 to 60 minutes, in the presence of from 0.1 to 50 weight percent of hydrogen donor material, based on the heavy residual oil.
6. A process according to any one of Claims 1 to 5, wherein the organic sulfur compound is selected from thiophenol, dodecanethiol and benzoethiophene.
7. A process according to any one of Claims 1 to 6, which is carried out in the absence of free hydrogen.

Patentansprüche

1. Verfahren zum Visbreaking eines schweren Erdölrückstandsöls, welches umfaßt:
 - (a) Zugabe einer organischen Schwefelverbindung mit einer aktiven Thiolkomponente zum Rückstandsöl vor dem
 - (b) Visbreaking des Rückstandsöls in Gegenwart eines stark aromatischen Wasserstoffdonator-Materials mit einem Gehalt an H_{Ar} - und H_{α} -Wasserstoff von mindestens 20% des gesamten Wasserstoff-

donator-Wasserstoffgehalts und Rückgewinnung eines Heizölprodukts mit einer Viskosität, die geringer als die des Ausgangsrückstandsöls ist.

2. Verfahren nach Anspruch 1, worin der Gehalt an H_{Ar} -Wasserstoff von 20 bis 50% beträgt und der Gehalt an H_v -Wasserstoff von 20 bis 50%, bezogen auf den gesamten Wasserstoffgehalt.

5 3. Verfahren nach Anspruch 2, worin das Wasserstoffdonator-Lösungsmittel einen H_v -Gehalt von mindestens 1,9 Gew.-% und einen H_{Ar} -Gehalt von mindestens 2,0 Gew.-% aufweist.

4. Verfahren nach einem der Ansprüche 1 bis 3, worin das Wasserstoffdonator-Material ein Rückstand der Hauptkolonne vom FCC, eine geklärte Ölaufschlammung, ein Rückstand von Syntower vom TCC, ein SRC-Kreislauföl oder ein leichtes Kreislauföl ist.

10 5. Verfahren nach einem der Ansprüche 1 bis 4, worin das Visbreaking bei einer Temperatur von 350 bis 485°C und einer Verweilzeit von 1 bis 60 Minuten in Gegenwart von 0,1 bis 50 Gew.-% des Wasserstoffdonator-Materials, bezogen auf das schwere Rückstandsöl durchgeführt wird.

6. Verfahren nach einem der Ansprüche 1 bis 5, worin die organische Schwefelverbindung aus Thiophenol, Dodecanthiol und Benzothiophen ausgewählt ist.

15 7. Verfahren nach einem der Ansprüche 1 bis 6, das in Abwesenheit von freiem Wasserstoff durchgeführt wird.

Revendications

20 1. Un Procédé de viscoréduction d'une huile résiduaire pétrolière lourde consistant à:
(a) ajouter à l'huile résiduaire un dérivé organique du soufre comportant un composant thiol actif avant de

(b) réduire la viscosité de l'huile résiduaire en présence d'un matériau donneur d'hydrogène hautement aromatique présentant une teneur en hydrogène H_{Ar} et en hydrogène H_{alpha} d'au moins 20% en poids par rapport à la teneur totale en hydrogène du donneur d'hydrogène et à récupérer un fuel oil d'une viscosité inférieure à celle de l'huile résiduaire de départ.

25 2. Un procédé selon la revendication 1, dans lequel la teneur en hydrogène H_{Ar} est comprise entre 20 et 50% et la teneur en hydrogène H_{alpha} est comprise entre 20 et 50% par rapport à la teneur totale en hydrogène.

30 3. Un Procédé selon la revendication 2, dans lequel le solvant donneur d'hydrogène présente une teneur en H_{alpha} d'au moins 1,9% en poids et une teneur en H_{Ar} d'au moins 2,0% en poids.

4. Un procédé selon l'une quelconque des revendications 1 à 3, dans lequel le matériau donneur d'hydrogène est un fond de colonne principale FCC, une huile de bouillie clarifiée, un fond de Syntower TCC, une huile de recyclage SRC ou une huile de recyclage légère.

35 5. Un procédé selon l'une quelconque des revendications 1 à 4, dans lequel la viscoréduction est mise en oeuvre à une température de 350 à 485°C et pendant un temps de séjour de 1 à 60 minutes, en présence de 0,1 à 50% en poids de matériau donneur d'hydrogène par rapport au poids de l'huile résiduaire lourde.

6. Un procédé selon l'une quelconque des revendications 1 à 5, dans lequel le dérivé organique du soufre est choisi parmi; thiophénol, dodécaneethiol et benzothiophène.

40 7. Un procédé selon l'une quelconque des revendications 1 à 6, qui est mis en oeuvre en l'absence d'hydrogène libre.

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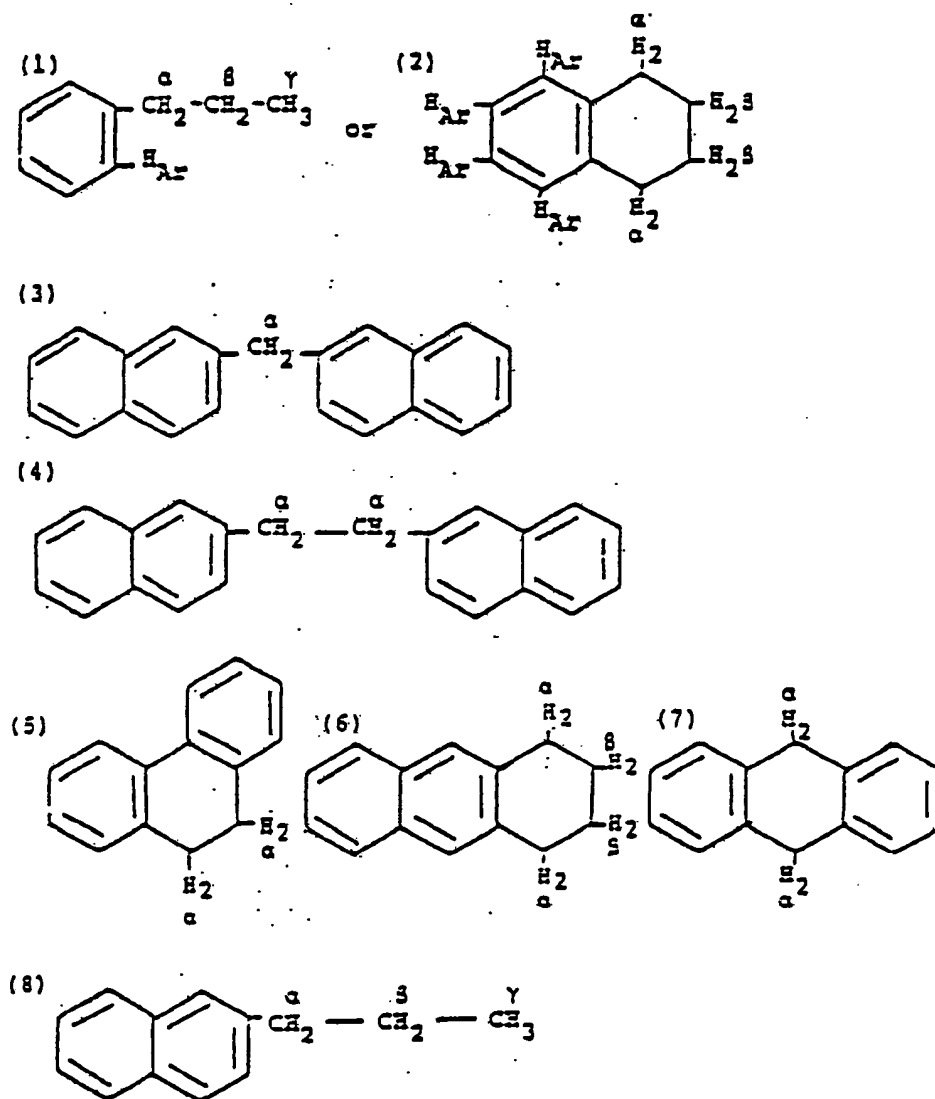


Fig. 1

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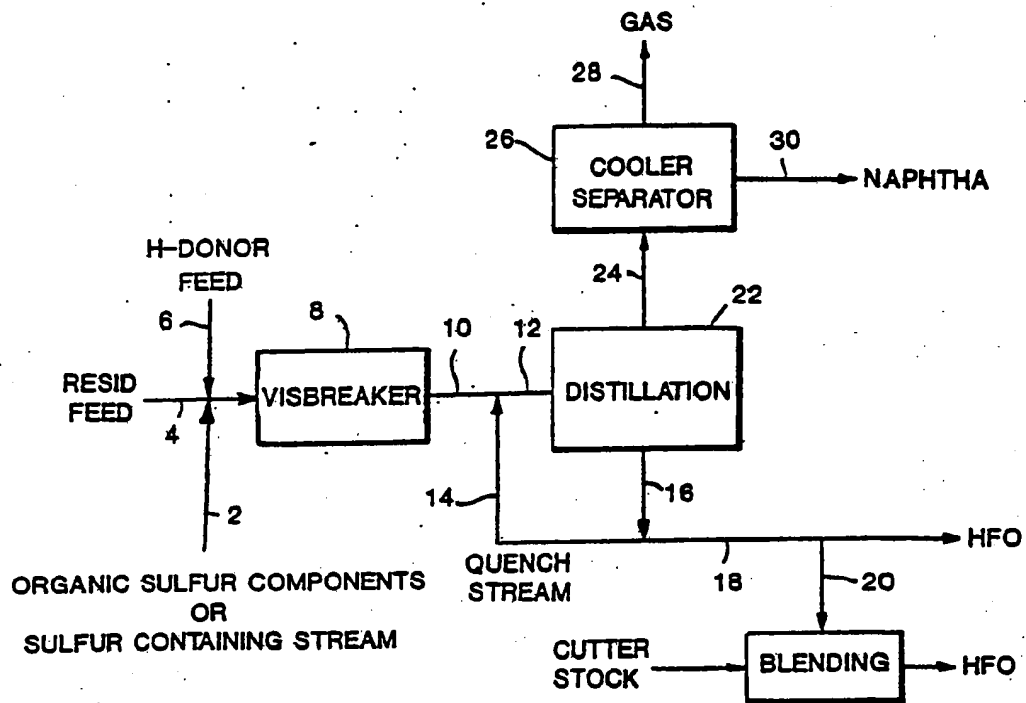


Fig. 2

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